

RENEWABLE FUELS FROM THE GASIFICATION OF FOOD AND AGRICULTURAL WASTES

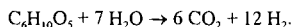
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INTRODUCTION

Renewable fuels can be produced from biomass feedstocks such as food and agricultural wastes at a competitive price. One method of achieving this goal is the steam reforming of biomass (Antal, 1975):



In this idealized, stoichiometric equation, cellulose (represented as $\text{C}_6\text{H}_{10}\text{O}_5$) reacts with water to produce hydrogen and carbon dioxide, mimicking the commercial manufacture of hydrogen from methane by catalytic steam reforming chemistry. More realistically, a practical technology must be able to convert the cellulose, hemicellulose, lignin, and extractive components of the biomass feedstock to a gas rich in hydrogen and carbon dioxide, including some methane and carbon monoxide. Unfortunately, biomass does not react directly with steam to produce the desired products. Instead, significant amounts of tar and char are formed, and the gas contains higher hydrocarbons in addition to the desired light gases (Antal, 1978, 1983, 1985). The recent work of Corella and his colleagues (Herguido et al., 1992) nicely illustrated this situation. In a fluid bed operating at atmospheric pressure Corella's group observed yields of char from the steam gasification of wood sawdust in the range of 20 to 10 wt %, and yields of tar decreasing to 4 wt % as the temperature of the bed increased from 650 to 775 °C. But at the highest temperature, only 80% of the carbon in the feedstock is converted to gas. By employing a secondary, fluidized bed of calcined dolomite operating at 800 to 875 °C, Corella and his co-workers (Delgado et al., 1997) were able to convert almost all of the tar to gas. Nevertheless, the char byproduct was not converted and represents an effective loss of gas.

The objective of this work is to define conditions which enable the steam reforming of biomass feedstocks such as food and agricultural wastes to produce renewable fuels.

EXPERIMENTAL

The gasification reactor (see Figure 1) is fabricated from Hastelloy C276 tubing with 9.53 mm OD x 6.22 mm ID x 1.016 m length (Xu et al., 1996; Matsumura et al., 1997). The feedstock is quickly heated by an annulus heater (located along the reactor's centerline) and an entrance heater outside the reactor to temperatures above 650 °C. The annulus heater (3.18 mm OD x 15.2 cm heated length) delivers all its heat directly to the feed. The entrance heater is made from a split stainless steel tube that is held in good thermal contact with the reactor, and an electrical heater coiled around the outer surface of the stainless steel tube. Downstream of the entrance heater, the reactor's temperature is maintained in an isothermal condition by a furnace. The chief purpose of the furnace is to prevent heat loss. Most of the heat required to lift the feedstock flow to reaction temperature is provided by the entrance heater and the annulus heater. Carbon catalyst is usually packed in about 60% of the heated zone of the reactor, as well as to the downstream cold section of the reactor. The reactor's temperature profile is monitored by 12 fixed, type K thermocouples held in good thermal contact with the reactor along its outer wall. The feedstock reaches to a peak temperature at the end of the heat up/cracking zone. Pressure in the reactor is measured by an Omega PX302 pressure transducer. A Grove Mity-Mite model 91 back-pressure regulator reduces the pressure of the cold, two-phase, product effluent from 28 to 0.1 MPa. After leaving the back-pressure regulator, the reaction products pass through a gas-liquid separator. The liquid product is collected over a measured time period to calculate the liquid outlet flow rate. The gas flow rate is measured using a wet test meter.

The feedstock is usually made of about 10 wt% biomass with about 4 wt% corn starch. The biomass is ground with a Wiley mill (Thomas Scientific) to 40 mesh before mixed with corn starch to form a paste. The feeder consists of a cylinder, a movable piston, and two end-caps (High Pressure Equipment). The cylinder is first filled with the paste feedstock, then the piston is placed on top of the feed, and the two end-caps are installed. Both the feeder and the reactor are pressurized separately to 28 MPa at the beginning of a run. During the time that the system is being brought up to temperature, water is pumped into the reactor by a Waters 510 HPLC pump. When the main body of the reactor reaches the desired temperature (usually about 650 °C), the feeder is connected to the reactor. Thereafter, water flow to the reactor is terminated, and water flow to the feeder is initiated, displacing the paste feedstock into the reactor. Because the thermophysical properties of the paste are considerably different than those of water, and possibly also because of exothermic pyrolysis reactions associated with the decomposition of the paste, the temperature of the feed rises very rapidly in the entrance region of the reactor. To

avoid excessively high temperatures, usually it is necessary to reduce the heat input to the feed from the annulus heater and the entrance heater.

Gas samples are taken by gas-tight syringes from the gas sample outlet of the separator. Analysis of the gas is conducted using a Hewlett-Packard model 5890 gas chromatograph equipped with flame ionization and thermal conductivity detectors. A 80/100 mesh carboxiphene molecular sieve packed column is used, operating at 35 °C for 4.2 min, followed by a 15 °C/min ramp to 227 °C, another ramp of 70 °C/min to 350 °C, and a 5 min hold at 350 °C. The carrier gas is a mixture of 8% hydrogen in helium (AIRCO). A standard gas mixture obtained from AIRCO is used for day-to-day calibration. The COD in the liquid effluent is determined by a HACH COD analyzer.

RESULTS AND DISCUSSION

The poplar wood sawdust paste was made by mixing sawdust into a starch gel. Large quantities of wood sawdust are available at \$30 per dry ton, and the quoted price of corn starch in bulk is \$0.12 per pound. Using these values, the price of a 10 wt% sawdust with 4 wt% starch paste is \$0.045 per pound. For comparison, the price of low sulfur coal is about \$0.025 per pound. Sawdust paste gasification results from two runs are displayed in Table 1. Complete gasification was achieved in both cases. The product gas was composed of mainly hydrogen, carbon dioxide, methane, and a trace of carbon monoxide. The gas product distribution was effectively identical between these two runs.

Table 2 displays results from the gasification of three feedstocks, sugar cane bagasse with corn starch, banagrass with corn starch, and onion with corn starch. In all three cases, the gas products consisted of about 28% hydrogen, 44% carbon dioxide, 24% methane, and 2% carbon monoxide, however, the runs with banagrass and onion were prone to plugging. As a result, the gas yield, and the carbon efficiency were significantly reduced due to carbon deposits on the reactor wall.

As mentioned earlier, carbon catalyst was usually packed in about 60% of the heated zone of the reactor. The reaction temperature reached to its peak value at the end of the heat up /cracking zone. Figure 2 shows the effect of peak temperature on the gasification of 10.6 wt% poplar wood sawdust with 4.0 wt% corn starch while keeping the catalyst bed temperature at 710°C. As the reactor peak temperature increased the hydrogen yield increased while the methane yield decreased, indicating high peak temperatures favored the methane steam reforming reaction.

To gain insight into the role of the reactor's wall as a catalyst for the steam reforming reaction, we wrapped the annulus heater with a nickel wire. We estimated that the surface area of the wire was about 30% of the surface area of the hot region of the reactor. As seen in Table 3, the results indicate that nickel has no special effect on the reaction chemistry. Molybdenum is another important component of Hastelloy, the alloy that the reactor is made of. To test its effect on the reaction chemistry, we mixed molybdenum powder with sawdust paste and delivered it to the reactor. The metal powder catalyzed char forming reactions which significantly reduced the gas yield, the carbon efficiency, and the global mass balance. Evidently, molybdenum is not a catalyst for the gasification reactions.

The liquid water effluent from the reactor usually has a neutral pH value, no color, and is odorless. Table 4 lists the COD (Chemical Oxygen Demand) measurements of the liquid effluent from the reactor. The mineral concentration of tap water was measured by drying tap water in an oven at 105°C. It is clear that there was only a trace of organics in the liquid effluent.

CONCLUSIONS

1. Onion, sugar cane bagasse, banagrass, poplar sawdust, and other food and agricultural wastes can be mixed into a corn starch gel (5 wt% or less) to form a thick paste. This paste is easily delivered to a supercritical flow reactor by a feeder.
2. Food and agricultural wastes can be steam reformed over a carbon catalyst to a gas composed of hydrogen, carbon dioxide, methane, and a trace of carbon monoxide. The liquid water effluent from the reactor has a low COD value, neutral pH, no color, and is odorless.
3. Coconut shell activated carbon catalyst is effective for the conversion of organic feedstocks, however, nickel and molybdenum have no catalytic effect on the gasification reactions.
4. High peak temperatures favor the methane steam reforming reaction.

ACKNOWLEDGEMENT

This work is Supported by NREL/DOE under cooperative agreement DE-FG36-94AL85804, and the Coral Industries Endowment of the University of Hawaii at Manoa. We thank Neil Rosmeissl (DOE), Dr. Ralph Overend (NREL), Dr. Patrick Takahashi and Dr. Richard Rocheleau (UH) for their interest in this work. The authors also thank Sonia Campbell (UH) and Dr. Heije Westberg (Chalmers University of Technology, Sweden) for their assistance with the experiments and discussion.

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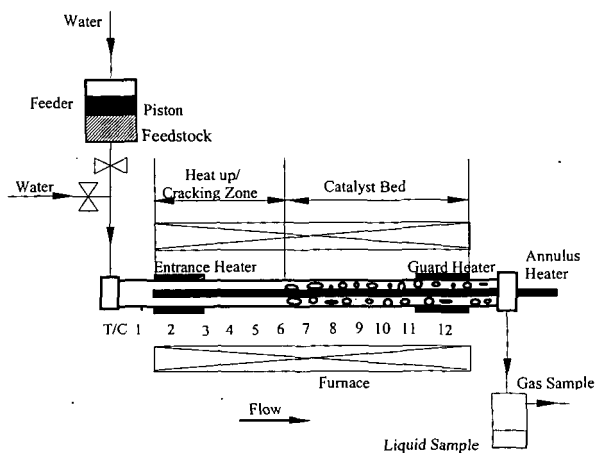


Figure 1. Gasification Reactor.

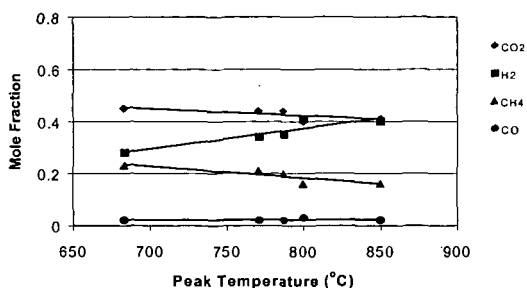


Figure 2. Effect of Peak Temperature on the Gasification of 10.6 wt% Poplar Wood Sawdust with 4.0 wt% Corn Starch (Catalyst Bed Temperature: 710°C).

Table 1. Gasification of Poplar Wood Sawdust /Corn Starch with Coconut Shell Activated Carbon Catalyst in Supercritical Water at 28 MPa.

| Experiment Date | 12/17/97 | 4/21/98 |
|---|--|---|
| Feedstocks (dry basis) | Sawdust 9.47 wt% + Corn Starch 3.55 wt% | Sawdust 10.64 wt% + Corn Starch 3.88 wt% |
| Reactor Peak Temp / Catalyst Bed Temp | 750°C/ 700°C | 739°C/ 710°C |
| Flow Rate (g/min) | 2.0 | |
| Time on Stream (hr) | 1.37 | 1.95 |
| Product | Mole Fraction | |
| H ₂ | 0.27 | 0.26 |
| CO | 0.02 | 0.02 |
| CO ₂ | 0.46 | 0.46 |
| CH ₄ | 0.24 | 0.23 |
| Total Gas Yield (L gas /g solid in feed) | 1.36 | 1.15 |
| (g gas /g solid in feed) | 1.34 | 1.21 |
| C Efficiency | 0.98 | 0.96 |
| Global Mass Balance | 0.95 | 1.00 |

Table 2. Gasification of Food and Agricultural Wastes with Coconut Shell Activated Carbon Catalyst in Supercritical Water at 28 MPa.

| Experiment Date | 5/6/98 | 6/3/98 | 6/24/98 |
|---|--|---|---|
| Feedstock (dry basis) | Sugar cane bagasse 10.70 wt% + Corn starch 4.28 wt% | Banagrass 11.70 wt% + Corn starch 4.60 wt% | Onion 11.10 wt% + Corn starch 4.20 wt% |
| Flow Rate (g/min) | 2.0 | | |
| Reactor Peak Temp / Catalyst Bed Temp | 749°C/ 716°C | 751°C/ 717°C | 750°C/ 716°C |
| Time on Stream (hr) | 1.23 | 0.73 | 0.96 |
| Product | Mole Fraction | | |
| H ₂ | 0.28 | 0.30 | 0.28 |
| CO | 0.02 | 0.02 | 0.02 |
| CO ₂ | 0.44 | 0.44 | 0.44 |
| CH ₄ | 0.23 | 0.24 | 0.25 |
| Total Gas Yield (L gas /g solid in feed) | 1.16 | 1.02 | 1.06 |
| (g gas /g solid in feed) | 1.22 | 1.02 | 1.02 |
| C Efficiency | 0.97 | 0.72 | 0.80 |
| Global Mass Balance | 1.02 | 0.93 | 0.92 |

Table 3. Effect of Metal Catalyst on the Gasification of Poplar Wood Sawdust / Corn Starch in a Reactor with a Packed Coconut Shell Activated Carbon Bed in Supercritical Water at 28 MPa.

| Experiment Date | 2/12/98 | 2/19/98 | 12/17/97 |
|--|--|--|---|
| Feedstocks (dry basis) | Sawdust 10.04 wt% + Corn Starch 3.65 wt% | Sawdust 10.5 wt% + Corn Starch 3.8 wt% | Sawdust 9.47 wt% + Corn Starch 3.55 wt% |
| Metal Catalyst | Ni Wire (wrapped around annulus heater) | Mo Powder (mixed in the Feedstock) | None |
| Reactor Peak Temp / Catalyst Bed Temp | 740°C/ 715°C | 730°C/ 680°C | 750°C/ 700°C |
| Flow Rate (g/min) | 2.0 | | |
| Time on Stream (hr) | 1.53 | 0.60 | 1.37 |
| Product | Mole Fraction | | |
| H ₂ | 0.31 | 0.29 | 0.27 |
| CO | 0.02 | 0.02 | 0.02 |
| CO ₂ | 0.42 | 0.46 | 0.46 |
| CH ₄ | 0.24 | 0.21 | 0.24 |
| Total Gas Yield | | | |
| (L gas/g solid in feed) | 1.16 | 0.90 | 1.36 |
| (g gas/g solid in feed) | 1.22 | 0.90 | 1.34 |
| C Efficiency | 0.91 | 0.66 | 0.98 |
| Global Mass Balance | 0.97 | 0.89 | 0.95 |

Table 4. COD Measurements of the Liquid Effluent from the Reactor.

| Experiment Date | Feedstock | COD in Liquid Effluent |
|-----------------|--------------------------------|-----------------------------------|
| 4/21/98 | Poplar Sawdust /Corn Starch | 56 mg/L |
| 6/24/98 | Onion /Corn Starch | 64 mg/L |
| 8/10/98 | Tap Water | Mineral Concentration 250 mg/L |